

Claims:

- 1 A method of polymerising ethylenically unsaturated monomers in which at least one ethylenically unsaturated monomer is polymerised using a catalyst system having a manganese carbonyl radical initiator, a halogen containing reactive substrate and an allylic halogen substituted chain termination agent.
- 5 2 A method as claimed in claim 1 wherein the initiator is or includes a compound of the formula (I):
- $$R^1-Mn(CO)_n(Lig)_p \quad (I)$$
- where
- 10 R^1 is C_1 to C_{30} hydrocarbyl, or hydrocarbyl substituted with halogen, alkyl, alkoxy, acyl; or
- R^1 is a group of the formula: $-Mn(CO)_n(Lig)_p$ where Lig, n and p are as defined below; each Lig is a ligand species;
- n is from 1 to 5; and
- 15 p is from 0 to 4; such that $n + p = 5$.
- 3 A method as claimed in claim 2 wherein the initiator is or includes a compound of the formula (Ia):
- $$(Lig)_p(CO)_nMn-Mn(CO)_n(Lig)_p \quad (Ia)$$
- 20 where Lig, p and n are as defined for formula (I), such that $p + n = 5$.
- 4 A method as claimed in claim 3 wherein the initiator is dimanganese decacarbonyl.
- 5 A method as claimed in any one of claims 1 to 4 wherein the an allylic halogen substituted chain termination agent is a compound of the formula (II):
- $$Hal-CHR^3-CR^4=CH_2 \quad (II)$$
- 25 where
- Hal is halogen; and
- R^3 and R^4 are each independently hydrogen, or a group: $(Link)_n-R^5$, where:
- n is 0 or 1,
- 30 Link is a linking group; and
- R^5 is halogen, glycidyl, an ethylenic double bond, carbonyl, carboxyl, cyano, hydroxyl, amino or quaternary amino or ammonium, a phosphorus containing species, a sulphur containing species, a hydrogen bond donor or acceptor, an aromatic ring, a heterocyclic ring, or a saccharide residue.
- 35 6 A method as claimed in claim 5 wherein Hal is a chlorine or bromine atom.

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- 7 A method as claimed in any one of claims 1 to 6 wherein the reactive substrate is also a chain terminating agent.
- 8 A method as claimed in any one of claims 1 to 6 wherein the reactive substrate is or includes a halogen substituted alkane, alcohol or carboxylic acid ester, an aromatic substituted alkyl
- 5 halide, a ring substituted benzyl halide, or a sulphonyl halide.
- 9 A method as claimed in claim 8 wherein the reactive substrate has multiple halogen substitution.
- 10 A method as claimed in claim 8 wherein the reactive substrate is or includes carbon tetrachloride, carbon tetrabromide, chlorotribromomethane, trichloromethane,
- 10 tribromomethane, dichloromethane, dibromomethane, 1,1-dichloroethane, 1,1-dibromoethane, 1,1,1-trichloroethane, 1,1,1-tribromoethane, 2,2-dichloroethanol, 2,2-dibromoethanol, 2,2,2-trichloroethanol, 2,2,2-tribromoethanol, trichloroacetic acid, C₁ to C₆ alkyl esters of trichloroacetic acid, C₂ to C₆ alkyl 2-bromo-2-methyl propionates, benzyl halides, 2-halo-2-phenylethanes, 4-alkyl benzyl halides, 4-fluorobenzyl bromide,
- 15 4-chlorobenzyl bromide, 4-fluorobenzyl chloride, 4-chlorobenzyl chloride, 1,2-di(bromomethyl)benzene, benzene sulphonyl chloride and toluene sulphonyl chloride.
- 11 A method as claimed in any one of claims 1 to 10 wherein the monomer is or includes one or more of an acrylic monomer, vinyl acetate, vinyl halide, styrene, α -methyl styrene, vinyl toluene; vinyl caprolactone, vinyl caprolactam or *N*-vinyl pyrrolidone.
- 20 12 A method as claimed in claim 11 wherein the monomer includes at least 40 mole% of acrylic monomer or monomers.
- 13 A method as claimed in either claim 11 or claim 12 wherein the acrylic monomer is or includes monomer of the formula (IV):
- $$\text{R}^{10}\text{-CR}^{11}\text{=CR}^{12}\text{-COR}^{13} \quad (\text{IV})$$
- 25 where
- R¹⁰ is methyl or, and desirably, hydrogen;
- R¹¹ is methyl or, and desirably, hydrogen;
- R¹² is methyl or hydrogen;
- provided that at least one of R¹¹ and R¹² is hydrogen, and
- 30 R¹³ is -OR¹⁴, or -NR¹⁵R¹⁶ where R¹⁴, R¹⁵ and R¹⁶ are each hydrogen, hydrocarbyl, or a polyalkyleneoxy chain.
- 14 A method as claimed in claim 13 wherein the monomer is or includes one or more acrylate or methacrylate ester; acrylic or methacrylic acid; acylyc or methacrylic amide; or a sulphonated acrylic monomer.

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- 15 A method as claimed in any one of claims 1 to 14 wherein the reaction conditions include heating the reaction mixture containing the manganese carbonyl radical initiator to initiate thermolysis of the initiator.
- 16 A method as claimed in claim 15 wherein the reaction is carried out at a temperature of from
5 50 to 150°C, particularly 50 to 100°C.
- 17 A method as claimed in any one of claims 1 to 16 wherein the reaction conditions include exposing the reaction mixture containing the manganese carbonyl radical initiator to actinic radiation to initiate photolysis of the initiator.
- 18 A method as claimed in claim 17 wherein the actinic radiation is visible or ultraviolet light.
- 10 19 A method as claimed in either claim 17 or claim 18 wherein the reaction is carried out at a temperature of from -50 to 100°C.
- 20 A method as claimed in any one of claims 1 to 16 wherein the reaction mixture additionally includes a Lewis acid, particularly a metal containing Lewis acid.
- 21 A method as claimed in claim 20 wherein the Lewis acid is a magnesium salt, particularly a
15 magnesium halide, such as magnesium bromide or magnesium chloride, a zinc salt, particularly a zinc halide, such as zinc bromide or zinc chloride, or zinc trifluoromethanesulfonate, a lanthanum salt such as lanthanum acetate, particularly as the heptahydrate, a ytterbium salt such as a ytterbium halide, particularly ytterbium chloride, or ytterbium triflate.
- 20 22 A catalyst system for polymerising ethylenically unsaturated monomers which is a combination of a manganese carbonyl radical initiator, a halogen containing reactive substrate and an allylic halogen substituted chain termination agent.
- 23 A catalyst system as claimed in claim 22 wherein the initiator is or includes a compound as defined in any one of claims 2 to 4.
- 25 24 A catalyst system as claimed in either claim 22 or claim 23 wherein the chain terminating agent is or includes a compound as defined in any one of claims 5 to 7.
- 25 A catalyst system as claimed in any one of claims 22 to 24 wherein the reactive substrate is also a chain terminating agent.
- 26 A catalyst system as claimed in any one of claims 22 to 24 wherein the reactive substrate is
30 or includes a compound as defined in any one of claims 8 to 10.
- 27 A catalyst system as claimed in any one of claims 22 to 24 which additionally includes a Lewis acid, particularly a metal containing Lewis acid.
- 28 A catalyst system as claimed in claim 27 wherein the Lewis acid is a magnesium salt, particularly a magnesium halide, such as magnesium bromide or magnesium chloride, a zinc

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salt, particularly a zinc halide, such as zinc bromide or zinc chloride, or zinc trifluoromethanesulfonate, a lanthanum salt such as lanthanum acetate, particularly as the heptahydrate, a ytterbium salt such as a ytterbium halide, particularly ytterbium chloride, or ytterbium triflate.

- 5 29 A polymer or copolymer of one or more ethylenically unsaturated monomers having at one end of the (co)polymeric chain a residue of a reactive substrate and a residue of a chain terminating agent at the other.
- 30 A polymer or copolymer as claimed in claim 29 wherein the (co)polymeric chain includes residues of one or more monomers as defined in any one of claims 11 to 14.
- 10 31 A polymer or copolymer as claimed in either claim 29 or claim 30 wherein the residue of the chain terminating agent is or includes the residue of a chain terminating agent as defined in any one of claims 5 to 7.
- 32 A polymer or copolymer as claimed in any one of claims 29 to 31 wherein the residue of the reactive substrate is or includes the residue of a reactive substrate as defined in any one of
- 15 claims 8 to 10.